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A STUDY OF MECHANISM OF FILM FORMATION IN GAS ABSORPTION ¹

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Much has been written about the mechanism of gas absorption and many theories have been formulated to account for the behavior of gases in contact with liquids. This paper deals, primarily, with gases during the first few seconds of contact with solvent liquid, and from observation of these phenomena a theory has been evolved to account for the behavior of a gas when brought in contact with a liquid.

The first quantitative study of gas absorption was made by Hurter,⁴ who made a thorough study of absorption towers used in sulphuric acid plants. After trying three methods of absorption, namely, bubbling gas through liquid; dropping liquid through soluble gas; passing gas counter-current to liquid in a packed tower, he reached the following conclusions. (1) The slower the liquid passed down through the column, the greater the recovery of soluble gas. (2) The slower the gas velocity, the longer the time of contact and consequent greater recovery.

TABLE OF NOMENCLATURE

w = weight of gas absorbed in grams,

t = time in hours,

$\frac{dw}{dt}$ = rate of absorption of gas, in grams per hour,

P = pressure of soluble gas in millimeters,

P_a = total pressure in gas phase,

C = concentration of gas in liquid (mols. gas per mol. of solvent),

g , as subscript, refers to gas phase,

l , as subscript, refers to liquid phase,



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⁴ Hurter, *J. Soc. Chem. Ind.* Vol. 4, p. 639 (1885); *Ibid.*, Vol. 6, p. 707 (1887); *Ibid.*, Vol. 12, p. 227 (1893).

t , as subscript, refers to top of column,
 b , as subscript, refers to bottom of column,
 i , as subscript, refers to interface of gas and liquid phases,
 k , coefficient of gas absorption, based on ΔP in mm.,
 h , coefficient of gas absorption, based on ΔC in mols.,
 A = area of interface, sq. cm.,
 K = overall coefficient of gas absorption, grams/hr./sq. cm./mm. partial pressure difference,
 α = mean concentration of inert gas in gas phase, expressed as $\frac{\text{volume of inert gas}}{\text{grams of absorbable gas}}$,
 d = thickness of gas film,
 e = diffusion coefficient of gas film,
 D = a constant,
 E = a constant,
 ρ = density of pure absorbable gas, grams per c.c.

Lewis,⁵ from his studies of a packed coke column, developed a mathematical expression for both extraction and absorption. He came to the conclusion that the rate of absorption, $\frac{dw}{dt}$ was directly proportional to the driving force. Further than this, the driving force was equivalent to the logarithmic mean of the differences in partial pressures of the soluble gas in liquid and gas phases at top and bottom of column. The final equation developed by Lewis was:

$$\frac{dw}{dt} = \frac{KA(P_{gt} - P_{lt}) - (P_{gb} - P_{lb})}{\log_e \left(\frac{P_{gt} - P_{lt}}{P_{gb} - P_{lb}} \right)} \quad (1)$$

Becker⁶ studied the rate of aeration of water deaerated by ferrous sulphate and proved that rate of stirring had a great effect upon the rate of solution. However, as the rate of stirring increased, the rate of solution did not increase proportionately, but asymptotically approached a maximum.

Among the first publications dealing with two film resistances to the transfer of material from one phase to another are those of Whitman and Keats⁷ and Lewis and Whitman.⁸ Their theory, based on experiments in both absorption and heat transfer, assumed:

⁵ Lewis, *J. Ind. and Eng. Chem.*, Vol. 8, p. 825 (1916).

⁶ Becker, *J. Ind. & Eng. Chem. Absorption Symposium* (1924).

⁷ Whitman and Keats, *J. Ind. & Eng. Chem.*, Vol. 14, p. 186 (1922).

⁸ Lewis and Whitman, *J. Ind. & Eng. Chem.*, Vol. 16, p. 1215 (1924).

(1) That the reaction rate was infinite when compared to the rate of diffusion of the products to and from the reaction zone.

(2) There were more or less defined layers on the two sides of the interface.

(3) The main bodies of both liquid and gas were each of uniform composition throughout, due to convection. The surface films then became the resistances to absorption, as owing to their stationary nature transfer through them took place only by diffusion. The rate of diffusion through the gas film was proportional to the driving force or to the difference in partial pressure of absorbable gas in main body of gas and partial pressure of this gas at the gas-liquid interface. The mathematical equations developed were:

$$\frac{dw}{dt} = Ak_g(P_g - P_i)$$

and

$$\frac{dw}{dt} = Ah_l(C_i - C_l),$$

where $(P_g - P_i)$ is the driving force between the gas phase and the interface, and $(C_i - C_l)$ is driving force between the interface and the liquid phase.

The calculation of the values of these coefficients was simplified by the assumption that a gas such as ammonia was so soluble that there was no appreciable gas pressure at the interface and substantially no resistance in the liquid film. Therefore, in this simple case the equation reduces to $\frac{dw}{dt} = Ak_g(P_g)$. In the case of the relatively insoluble gases, a liquid film or partially saturated layer resulted, through which the gas diffused before reaching the main body of the solution, and the equation was $\frac{dw}{dt} = k_l A(C_g - C_l)$.

Numerical values of the film coefficients k_g and k_l for various gases are given in the original paper. The over-all absorption coefficients for any piece of equipment could be determined from these film coefficients, which are the constants denoting the rate of absorption.

It is evident that many factors affect the over-all absorption coefficient, and an investigation of some of these factors, namely time and rate of stirring, was undertaken to further determine the validity of the two film theory.

APPARATUS

The apparatus used for studying absorption rates is shown in Figure 1. It is similar to that used by Wroblewski⁹ and again by Becker⁶ when observing rate of solution of gases in quiescent liquids. In the present case agitated liquids were to be studied, as

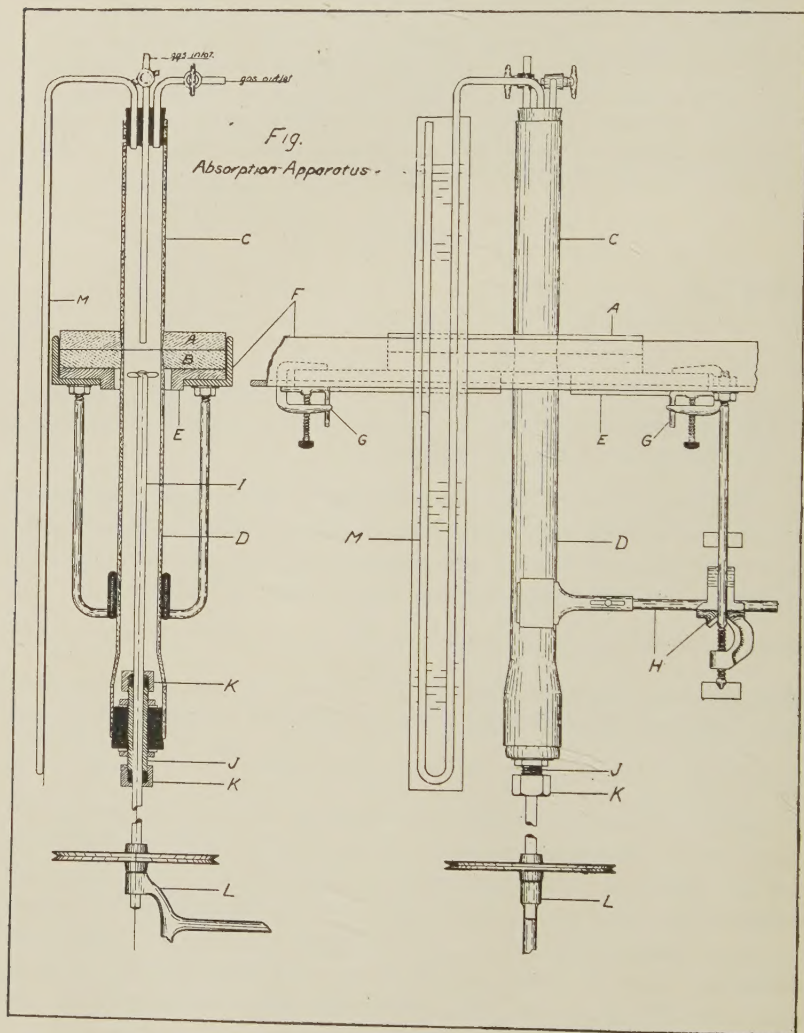


FIG. 1. Apparatus used in determining rate of absorption.

⁹ Wroblewski, *Ann. Physik*, Vol. 4, p. 268 (1878).

well as still liquids, and for this purpose a stirrer was introduced from the bottom. This stirrer was the propeller type which gave good agitation without breaking the surface of the liquid.

In Figure 1, *A* and *B* represent two glass plates (4 x 6 x 7/16 inches) with ground glass surfaces forming a gas tight valve when slightly greased and slid apart. *C* and *D* are 1 inch glass tubes ground with a taper to fit corresponding holes in the plates. The liquid chamber *D* has a bell bottom to allow enough space to accommodate a brass bearing for the stirrer. *E* is a wooden block to which the smooth side of the lower glass plate was cemented with ambroid cement. The two plates of glass together with the wooden block were inserted between the angle irons *F* with the vertical sides of the angle irons acting as guides for the top sliding plate, as shown in the illustration. The stirrer *L* was made from a brass rod and a small piece of sheet brass. The brass bearing *J* was screwed into the rubber stopper and both inserted in bell bottom of tube *B*. The packing shown at *K* was ordinary candle-wicking thoroughly impregnated with lanolin. With the two supports, namely, the brass bearing in stopper and the stirrer bracket, little vibration was experienced with stirrer traveling at the rate of 324 r.p.m. The top tube or gas chamber *C* was closed by a three hole rubber stopper in which three tubes were inserted. One, the gas inlet extended nearly to the bottom of the chamber. Another tube served as a gas outlet. A manometer *M* was inserted through the third hole in the stopper. This apparatus when properly mounted was rigid and gas tight up to a vacuum of 350 mm. of mercury. Beyond this, air would enter through the packing gland in the bottom and cause errors in the results.

PROCEDURE

Before operating, it was necessary to determine the capacity of the two chambers. The capacity of the liquid chamber was determined with propeller in place and found to be 101 cc. of water. Measurement of gas chamber capacity was accomplished by filling the upper tube with water up to the stopcocks of both gas inlet and outlet. The mean value of the measured volume of water was 58.5 cc., to which was added the volume of manometer tube of 2.2 cc., making a total of 60.7 cc. These values were used in the computations.

As absorption rates of both pure and mixed gases were deter-

mined in this apparatus, some method had to be devised to analyze accurately small volumes of gas. A specially constructed gas pipette was used for this purpose. The pipette consisted of two pieces of glass tubing; one piece being 4 mm. in diameter by approximately 150 mm. long and the other piece about 7 mm. diameter by 210 mm. long. These two pieces were fused together forming a single tube. A two way glass stopcock was fused to the small end of the tube and a one way stopcock fused to the large end. Volume was read from a mm. scale etched on one side of the tube. This sampling pipette was used like a standard absorption burette, that is, the absorbed gas was displaced by absorbing liquid.

In preparing for a run, the gas chamber (Fig. 1) was removed, and the liquid chamber filled with distilled water through the coinciding holes in the two plates. The water level was brought just above the ground surface of the lower plate so that when the plates were slid apart the top plate cut off the top of the water column and no air was entrapped in the lower chamber. The water thus cut off was absorbed by filter paper. The gas chamber with inlet, outlet and manometer tubes was then fitted into place in the top plate. This chamber was flushed out with a mixture of gas and air, previously saturated with water vapor, until the gas leaving the chamber was of constant composition.

A run was started by sliding the two plates together so that the gas and liquid chambers communicated with each other. The liquid in the manometer tube immediately started to rise, due to reduction of pressure in gas chamber resulting from absorption of soluble gas. The rise of liquid in one arm of manometer was noted at 10 second intervals. These readings gave necessary data so that actual volumes of gas absorbed could be computed.

Rates of absorption were thus determined for three pure gases, and for various mixtures of ammonia and air. The amount of inert gas present was varied from 85 per cent to 0 per cent in order to determine the effect, if any, of dilution upon the phenomena taking place at and near the interface.

When pure or nearly pure gas was used and absorption was rapid, the gas chamber *C* was too small to give accurate readings. In order to overcome this difficulty, a larger auxiliary gas chamber was used. For lower concentrations than pure gas, a one liter bottle was used, and for a pure gas a two liter bottle served as the gas chamber. Careful flushing was needed to insure a uniform

mixture of gas in both $\bar{C}$ and the auxiliary chamber. Seven millimeter glass tubing with no stopcocks was used in the gas train to eliminate constrictions to the flow of gas. The enlarged gas chamber slowed down the rate of rise of liquid in the manometer considerably, and brought the readings into a range easily readable.

Another question presented itself in calculating the rate of absorption when using the large gas chamber. It is quite evident that there is much more gas absorbed in the case where large chambers were used and it was necessary to check up on the back pressure exerted by the dissolved gas. After calculating the amount of gas absorbed, it was found that even in the case of the pure ammonia gas, after three minutes time, the amount of gas absorbed was only 0.00246 gms. per gm. H_2O , which gives a partial pressure of 2 mm. or less. Due to this fact the back pressure was considered negligible and disregarded in the calculations.

The rate of stirring in all but two cases was 324 r.p.m. In these cases the rates were 280 and 376 r.p.m. To correct the rate of absorption for these differences in stirring, each absorption coefficient obtained was multiplied by the ratio of the two speeds, that is, by the factor $\frac{324}{280}$ for the case of slower stirring, and $\frac{324}{376}$ in case of the more rapid stirring. This correction is based upon the conclusions of Becker⁶ who found that when the rate of solution was plotted against the rate of stirring, a logarithmic curve was obtained which approached a maximum rate of solution asymptotically. However, the curve is almost a straight line and can be assumed so for such small differences in rate of stirring as 44 r.p.m.

RESULTS WITH AMMONIA (LIQUID STIRRED)

The results of the experiments on the absorption of ammonia into stirred liquid are presented as graphs in Tables I, II, and III and in Figs. 2, 3 and 4. As ammonia is an example of a very soluble gas and its behavior in absorption illustrates the film theory of absorption for the case where the liquid film resistance is negligible, a discussion of absorption of ammonia will be given in detail.

In curves of Figs. 2, 3, and 4 the overall rate of absorption K , is plotted against time for both stirred and unstirred liquid. These curves show that when ammonia is accompanied by an inert gas the value of K decreases considerably with the passage of time from the moment that the gas and liquid phases are brought in contact.

TABLE I

OVERALL COEFFICIENT FOR ABSORPTION OF AMMONIA IN WATER, WITH
LIQUID STIRRED

Mean values of K , expressed as grams $\times 10^{-4}$, per hour, per sq. cm. per mm. partial
pressure difference, over time interval given *

Time Interval Seconds	Initial Concentration of Gas Phase					
	17.5% NH ₃	29.2% NH ₃	56.2% NH ₃	88.9% NH ₃	98.1% NH ₃	100% NH ₃
0-10....	5.77	5.93	7.55	13.8	22.5	30.8
10-20....	3.04	3.14	4.40	7.53	16.3	30.2
20-30....	2.28	2.64	3.48	6.55	13.8	27.2
30-40....	1.82	2.30	2.98	5.17	11.0	29.4
40-50....	1.67	1.83	2.50	4.67	11.2	30.3
50-60....	1.52	1.69	2.70	3.89	9.53	29.0
60-70....	1.49	1.50	2.39	3.76	9.30	31.4
70-80....	1.47	1.59	2.30	4.02	6.90	29.4
80-90....	1.46	1.51		3.64	7.43	32.4
90-100....	1.44	1.55		3.13	6.99	29.7
100-110....	1.41	1.54		2.81	7.32	
110-120....				2.84	7.12	

* These data are plotted in Figure 2.

TABLE II

OVERALL COEFFICIENT FOR ABSORPTION OF AMMONIA IN WATER, WITH
LIQUID STIRRED

Mean values of K , expressed as grams $\times 10^{-4}$, per hour, per sq. cm. per mm. partial
pressure difference, over time interval given *

Time Interval Seconds	Initial Concentration of Gas Phase				
	33.4% NH ₃	55.7% NH ₃	87.7% NH ₃	98.6% NH ₃	100% NH ₃
0-10.....	6.2	7.07	12.9	25.6	29.2
10-20.....	3.46	4.09	9.31	17.7	28.2
20-30.....	2.54	3.46	7.70	12.9	29.0
30-40.....	2.46	2.68	5.64	11.8	29.9
40-50.....	2.23	2.83	6.12	10.4	30.6
50-60.....	2.34	2.22	5.07	10.6	29.0
60-70.....	1.81	2.31	4.23	9.46	30.0
70-80.....	1.90	1.99	4.25	9.60	31.8
80-90.....	1.98	1.80	2.87	9.30	32.2
90-100.....	1.71	1.69	3.43	8.68	31.2
100-110.....	1.42		2.62	7.92	31.8
110-120.....	1.40			7.55	29.2

* Plotted in Figure 3.

TABLE III

OVERALL COEFFICIENT FOR ABSORPTION OF AMMONIA IN WATER, WITH
LIQUID QUIESCENT.

Mean values of K , expressed as grams $\times 10^{-4}$, per hour, per sq. cm. per mm. partial
pressure difference, over time interval given *

Time Interval Seconds	Initial Concentration of Gas Phase				
	15.1% NH ₃	55.2% NH ₃	92.9% NH ₃	98.6% NH ₃	100% NH ₃
0-10.....	4.98	6.8	11.55	14.7	13.72
10-20.....	3.02	3.7	8.83	9.99	11.50
20-30.....	2.12	2.72	6.34	7.78	9.23
30-40.....	1.81	2.49	4.98	6.49	8.14
40-50.....	1.59	2.26	4.76	5.82	8.38
50-60.....	1.43	2.19	4.53	5.13	6.19
60-70.....	1.28	1.81	4.30	4.60	5.67
70-80.....	1.43	1.66	4.08	4.15	5.06
80-90.....	1.21	1.66	3.55	4.15	4.45
90-100.....	1.21	1.66	3.25	4.15	4.60
100-110.....		1.66	2.72	3.92	4.00
110-120.....			2.72	3.92	4.53

* Plotted in Figure 4.

Since these values of K take into consideration any change in the overall or apparent value of ΔP , a decrease in K is to be accounted for either by an increase in resistance with passage of time or by a decrease in the effective value of ΔP , or both.

It is further noted that when the gas phase is composed of pure ammonia (and water vapor) the value of K does not decrease with passage of time when the liquid is stirred. When as little as 1.4 per cent of inert gas is present in the gas phase it is noted that the rate falls off fully three-fourths as rapidly as when 12.3 per cent inert gas is initially present and five-eighths as rapidly as when 82.5 per cent inert gas is initially present. There is very little difference in the rate at which the absorption coefficient K decreases for mixtures in which the gas phase contains initially over 15 per cent inert gas. These data are of fundamental significance and will therefore be fully discussed.

The decrease in K is not to be accounted for by any phenomenon occurring within the liquid phase. The maximum amount of ammonia dissolved in any experiment would have created a solution not exceeding 0.24 per cent, having a corresponding vapor pressure of less than 2 mm., which is almost negligible. It is conceivable, however, that there may have been a more concentrated solution

at the surface of the liquid which would exert a correspondingly higher vapor pressure. It is also conceivable that the rapid rate of absorption of ammonia with consequent heat liberation may have raised the temperature of the liquid surface considerably above the temperature of the body of liquid phase which in turn would result in

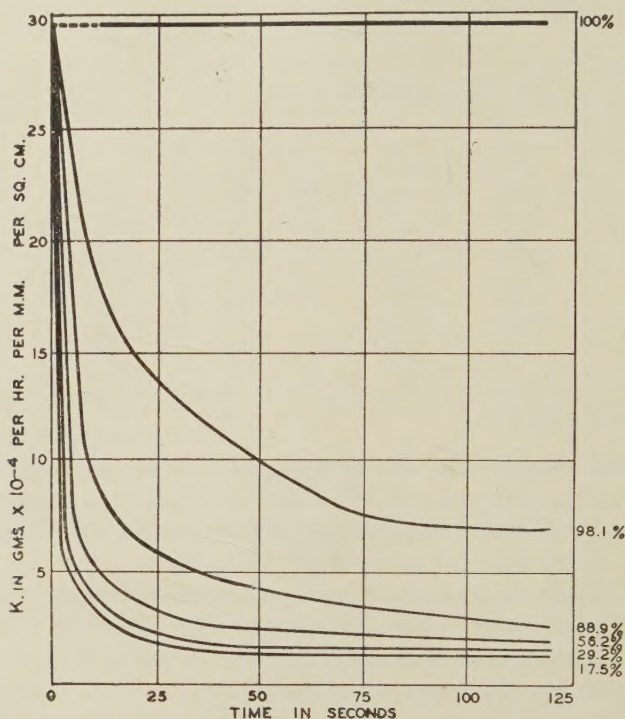


FIG. 2. Absorption coefficient for NH_3 liquid, stirred.

a higher vapor pressure from the surface of the liquid. If either of these possibilities were, in fact, responsible for decrease in K , then the decrease in K should have been most marked in the experiments in which there was no inert gas in gas phase. The results show that in the case where no inert gas was present, the value of K did not decrease but remained constant, and the conclusion is justified that there was no increase in temperature of surface of liquid, nor increase in concentration of surface of liquid sufficient to decrease the effective value of P .

The explanation for the decrease in K with passage of time must,

therefore, be in some change which takes place within the gas phase. It will be noticed that the value for K is the same for all concentrations of gas phase at the instant the gas and liquid phases are brought into contact. This eliminates any question as to whether the apparent value of ΔP is truly representative of the absorption tendency of the ammonia in gas and liquid phases before there has

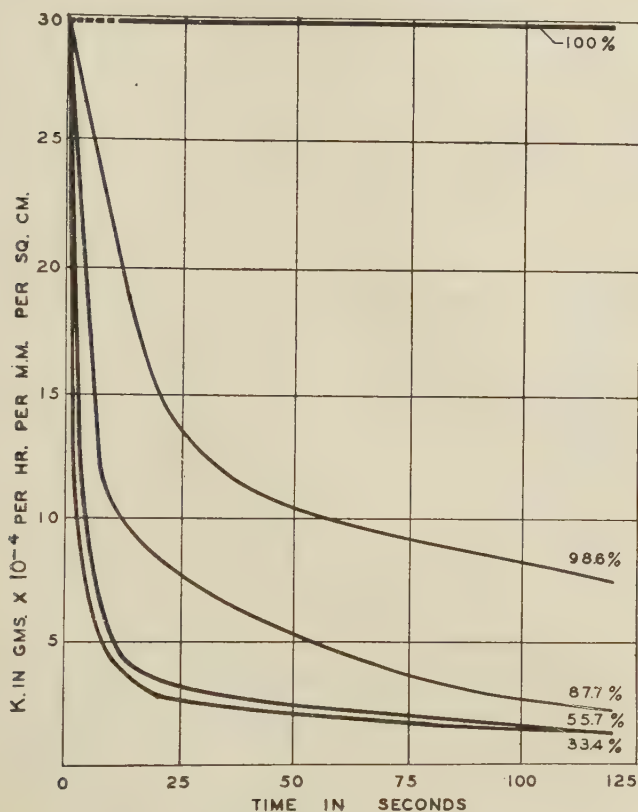


FIG. 3. Absorption coefficient for NH_3 liquid, stirred.

been an opportunity for the gas phase to undergo a change. It therefore follows that the decrease in value of K with passage of time is to be accounted for by the building up of a resistance to the passage of ammonia molecules from the body of the gas phase to the liquid surface. Various workers have recognized that some resistance in the gas phase will in certain cases limit the rate at

which a gas is dissolved by a liquid. Whitman and Keats designated this as a gas film. They and subsequent workers presented the view that this gas film was due to the presence of a substantially stationary layer of inert or non-absorbed gas at and near the liquid surface. They further assumed that the soluble gas passes through this layer by diffusion.

It appears that when a gas and liquid phase are first brought into contact absorption of the soluble gas results in a general

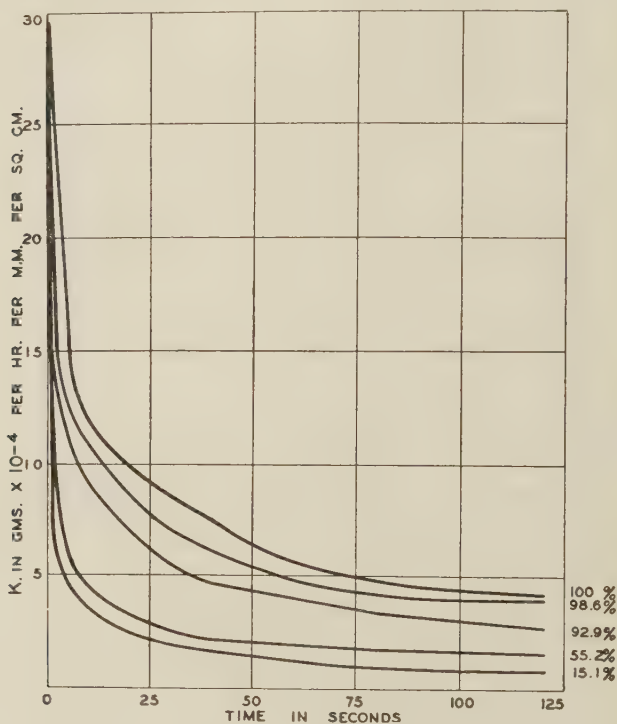


FIG. 4. Absorption coefficient for NH_3 liquid, quiet.

mechanical flow consisting of both inert and soluble gas toward the surface of the liquid. Soluble and inert gas may also be brought toward the surface of the liquid by convective currents which may, in part, be intentionally mechanically produced. Further, since the concentration of soluble gas is higher in the gas phase than at the liquid surface, soluble gas will move past inert gas, toward the liquid surface by the process of diffusion. Inert gas may move from the

surface of the liquid toward the body of the gas phase by diffusion and both inert and soluble gas will be moved from the liquid surface by convection. In any apparatus in which the convection currents are substantially constant, the rate of absorption will decrease with passage of time from the moment the gas and liquid phases are brought into contact until such time that the rate of movement of inert gas from liquid surface by process of diffusion and convection equals the rate at which inert gas is moved toward the surface by the processes of convection and the general flow of gas phase attendant on the absorption of soluble gas. The inert gas is therefore a factor not to be neglected. When no inert gas is present there is no resistance to absorption within the gas phase and the rate of absorption appears to be determined wholly by the difference in activity or partial pressure of the soluble gas at the surface of the liquid and body of the liquid phase. It is therefore possible to calculate the gas film resistance, or decrease in partial pressure difference of soluble gas in the body of gas phase and at the interface, from the overall coefficient obtained in experiments made with pure gas and a gas phase containing inert gas when liquid is both stirred and quiet. The calculation of conductance, the opposite of resistance, is given below.

It has been previously shown by Lewis and Whitman that

$$\frac{I}{K} = \frac{I}{k_g} + \frac{I}{k_l} \quad \text{or} \quad k_g = \frac{k_l \times K}{k_l - K}.$$

If k_l is known, it is possible to calculate k_g for various percentages of gas in the gas phase; and it is here that the data on absorption of ammonia, when liquid is still, become of value.

When 100 per cent ammonia gas is absorbed in still liquid the resistance which prevents instantaneous reaction must be due to two things: (a) The resistance of the liquid layer and (b) The actual resistance at the interface due to combination of gas molecules with liquid molecules to form ammonium hydroxide.

In Figs. 2 and 3, where 100 per cent gas is being dissolved, the total resistance must be taken up in a concentrated liquid layer and the reaction zone. The resistance due to combination of molecules is probably so small in comparison to the liquid layer that it can be neglected and is so neglected in these calculations. In the absorption of 100 per cent gas, k_l is assumed to have the same value as K , namely 0.00296 g./hr./sq. cm./mm. pp. NH_3 . If k_g is desired for

TABLE IV
CALCULATED VALUES OF GAS FILM COEFFICIENT

Values of k_g are expressed as $\text{grams} \times 10^{-4}$, per hour per sq. cm. per mm. partial pressure difference

Values calculated from data plotted in Fig. 2, Liquid Stirred

% NH ₃	10 sec.	20 sec.	30 sec.	40 sec.	50 sec.	60 sec.	70 sec.	80 sec.	90 sec.	100 sec.
98.1	50.8	30.	22.8	18.4	15.3	12.9	11.0	10.10	9.55	8.42
88.9	12.9	9.18	7.05	5.92	5.17	4.55	4.25	3.76	3.67	3.38
56.2	6.65	4.56	3.57	3.10	2.91	2.60	2.48	2.38	2.32	2.29
29.2	4.6	3.14	2.46	2.02	1.81	1.77	1.77	1.77	1.73	1.68
17.5	4.24	2.78	1.85	1.81	1.67	1.60	1.56	1.52	1.50	1.47

Values calculated from data plotted in Fig. 3, Liquid Stirred

% NH ₃	10 sec.	20 sec.	30 sec.	40 sec.	50 sec.	60 sec.	70 sec.	80 sec.	90 sec.	100 sec.
98.6	75.5	30.6	21.4	17.5	15.8	14.3	13.3	12.6	11.7	10.8
87.7	16.0	11.5	9.19	7.73	6.46	5.37	4.34	3.85	3.10	2.82
55.7	6.11	4.04	3.37	2.82	2.64	2.46	2.20	2.02	1.85	1.59
33.4	5.06	3.28	2.73	2.46	2.19	2.11	1.85	1.69	1.51	1.43

Values calculated from data plotted in Fig. 4, Liquid Quiescent

% NH ₃	10 sec.	20 sec.	30 sec.	40 sec.	50 sec.	60 sec.	70 sec.	80 sec.	90 sec.	100 sec.
98.6	227.	79.0	38.3	31.4	33.5	24.4	33.9	28.7	41.0	57.4
92.9	46.9	26.85	15.3	12.9	14.27	12.52	14.35	14.65	10.62	11.08
55.2	6.98	4.83	3.83	3.33	3.15	3.01	2.82	2.75	2.63	2.34
15.1	5.3	3.44	2.82	2.20	1.97	1.78	1.46	1.62	1.14	1.55

any percentage mixture of ammonia and air, k_l is known and k_g can be calculated. For example, in Figure 2 for the absorption of 98.1 per cent ammonia, at the end of 10 seconds the value of K is 0.00187 g./hr./sq. cm./mm. pp. NH_3 and k_l is 0.00296, assuming the value of the liquid coefficient does not change with change in concentration of gas phase.

$$k_g = \frac{0.00296 \times 0.00187}{0.00296 - 0.00187} = 0.00508.$$

In a similar manner the values of k_g for all percentage gas concentrations were calculated, and are given in Table IV.

RESULTS WITH AMMONIA (LIQUID QUIESCENT)

When liquid was not stirred the overall coefficient K , and also the liquid film coefficient k_l for a 100 per cent gas, both change due to a building up of a layer of liquid of higher concentration than before. In Figure 4 the initial value of K is shown to be the same as when the liquid is stirred, but at the end of 10 seconds for 100 per cent ammonia the value is 0.00117 as compared to the value of 0.00296 when liquid is stirred. As there can be no resistance in the gas phase on account of absence of inert molecules, the coefficient k_l can be assumed equal to K for 100 per cent gas in calculating the values of k_g for mixtures of ammonia and inert gas. The overall K for the 98.6 per cent mixture at the end of 10 seconds is 0.00111. Substituting in the formula given above,

$$k_g = \frac{0.00111 \times 0.00117}{0.00117 - 0.00111} = 0.0227 \text{ g./hr./sq. cm./mm. pp. } \text{NH}_3.$$

In like manner k_g was computed for various mixtures and at regular intervals of time. The calculated values of k_g are shown in Table IV.

One of the most notable tendencies of the data is the fact that the value of k_g decreases as the percentage of inert gas in the mixture increases. This tendency is apparent in the data pertaining to the stirred as well as the unstirred liquid. It can also be seen that the values of k_g decrease as time of contact of liquid and gas increase. This bears out the theory that the conductivity of the gas phase as a whole increases with purer gas and decreases with length of time of contact. These phenomena are caused by the interference of the molecules of inert gas causing a resistance to the

flow of soluble gas molecules as they make their way toward the liquid interface.

If the explanation offered for the mechanism of the formation of the gas film is correct, then during the earlier stages of gas film formation the gas film resistance should be substantially proportional to the amount of inert gas left adjacent to the interface coincident with the absorption of the soluble gas. However, after the film had increased to a certain thickness this would no longer be true, because of the increasing effect of convection on the outer surface of the film.

The conductance of the gas film, k_g may be expressed as

$$k_g = \frac{e}{d}$$

and

$$d = \frac{\alpha w}{A};$$

hence

$$k_g = \frac{eA}{\alpha w}$$

and

$$dw = - \frac{eA}{\alpha} \cdot \frac{dk_g}{k_g^2}. \quad (1)$$

But since

$$\frac{dw}{dt} = \frac{(\Delta P)A}{\frac{1}{k_l} + \frac{1}{k_g}} \quad (2)$$

if the value of dw from the equation (1) is substituted into equation (2) it follows that

$$\frac{-eA \cdot dk_g}{\alpha k_g^2 \cdot dt} = \frac{(\Delta P)A}{\frac{1}{k_l} + \frac{1}{k_g}}.$$

Simplifying and collecting terms

$$\begin{aligned} \frac{-dk_g}{k_g^2} \left(\frac{1}{k_l} + \frac{1}{k_g} \right) &= \frac{\alpha \cdot \Delta P}{e} \cdot dt \\ - \int \frac{dk_g}{k_l \cdot k_g^2} - \int \frac{dk_g}{k_g^3} &= \int \frac{\alpha \cdot \Delta P}{e} dt. \end{aligned}$$

Since k_l , α , ΔP , and e are constants during a run,

$$\frac{1}{k_l \cdot k_g} + \frac{1}{2k_g^2} = \frac{\alpha \cdot \Delta P}{e} t + B$$

and

$$\frac{1}{k_g} \left(\frac{1}{k_l} + \frac{1}{2k_g} \right) = \frac{\alpha \cdot \Delta P}{e} t + B,$$

when $t = 0$, $k_g = \infty$, therefore $B = 0$, and

$$\frac{\alpha \cdot \Delta P}{e} = \frac{1}{t \cdot k_g} \left(\frac{1}{k_l} + \frac{1}{2k_g} \right) = D, \quad (3)$$

where D is a constant.

Since, for these experiments, the vapor pressure of ammonia from the liquid was negligible,

$$D = \frac{\alpha \cdot \Delta P}{e} = \frac{P_a - P}{\rho P} \cdot \frac{P}{e} = \frac{P_a - P}{\rho e}.$$

$$\text{Hence, } \frac{D}{\text{partial pressure of inert gas}} = \frac{1}{\rho e}$$

and, since the experiments were made at substantially constant pressure.

$$\frac{D}{\text{mol. fraction inert gas}} = \frac{P_a}{\rho e} = E, \text{ where } E \text{ is a constant.} \quad (4)$$

The calculation of the values of the constant, D , by use of equation (3) may be illustrated by using the data for 98.1 per cent NH_3 , liquid stirred, at the end of 30 seconds. For this case,

$$K = 29.6 \times 10^{-4} = k_l,$$

$$k_g = 22.8 \times 10^{-4},$$

$$D = \frac{1}{t \cdot k_g} \left(\frac{1}{k_l} + \frac{1}{2k_g} \right) = \frac{3600}{30 \times 22.8 \times 10^{-4}} \left(\frac{1}{29.6 \times 10^{-4}} + \frac{1}{2 \times 22.8 \times 10^{-4}} \right) \\ = 0.294 \times 10^8.$$

Values of D so calculated are tabulated in Table V. In general it will be noted that for each run constant values of D are obtained for some seconds, and that the values then decrease. Though in some instances the data are erratic, fairly constant values of D were obtained for the first 50 seconds that gas and liquid were in contact. The average values of D , for each case, for the first 50 seconds were used to calculate the values of the constant E , by means of equation (4). Thus for the run for 98.1 per cent NH_3 , the "average" constant value of D was 0.305×10^8 . Therefore,

$$E = \frac{D}{\text{mol. fraction of } \text{NH}_3} = \frac{0.305 \times 10^8}{1.00 - 0.981} = 16.1 \times 10^8.$$

TABLE V.
CALCULATED VALUES OF CONSTANTS, $D \times 10^8$ AND $E \times 10^8$
For Indicated Percents of NH_3 in Gas Phase

Time Seconds	Values of D from data from Fig. 2				Values of D from data from Fig. 3					Values of D from data from Fig. 4			
	17.5%	29.2%	56.2%	88.9%	98.1%	33.4%	55.7%	87.7%	98.6%	15.1%	55.2%	92.9%	98.6%
10.....	12.9	11.2	5.91	2.01	0.310	9.38	6.78	1.46	0.192	12.1	7.96	0.729	0.137
20.....	13.8	11.1	5.66	1.73	0.303	10.2	7.00	1.20	0.292	12.8	7.50	0.796	0.241
30.....	11.7	11.6	5.84	1.79	0.294	9.20	6.46	1.15	0.322	12.4	7.68	1.16	0.402
40.....	15.4	12.5	5.66	1.79	0.299	8.66	6.73	1.13	0.319	14.9	7.76	1.22	0.438
50.....	14.4	12.3	5.10	1.81	0.314	8.58	6.08	1.23	0.296	15.0	7.24	0.98	0.374
60.....	13.0	11.7	5.24	1.90	0.331	7.86	5.78	1.41	0.288	15.5	6.86	1.05	0.456
70.....	11.7	9.2	4.89	1.83	0.372	8.43	6.10	1.76	0.274	19.1	6.86	0.84	0.326
80.....	10.7	8.2	4.63	1.99	0.372	8.74	6.28	1.91	0.260	14.6	6.53	0.77	0.368
90.....	9.8	7.5	4.30	1.86	0.368	9.66	6.56	2.51	0.258	23.4	6.34	1.03	0.234
100.....	9.2	7.1	3.98	1.93	0.343	9.61	7.86	2.69	0.266	13.2	7.04	0.94	0.159
$D \times 10^8$ *.	13.6	11.8	5.63	1.82	0.395	9.20	6.61	1.24	0.280	13.5	7.63	0.977	0.318
$E \times 10^8$...	16.5	16.7	12.8	16.4	16.1	13.8	14.9	10.1	20.0	15.9	17.0	13.8	22.7

* Average value of D for first 50 seconds.

The values of E for all the runs are given in Table V. The average value of E for all runs was 15.6, and while three runs show a variation of 28 per cent to 39 per cent from the mean value, the remaining 10 runs give satisfactorily concordant results. It may therefore be concluded that the theory offered as an explanation of the mechanism of film formation brings into harmony the various values for the overall coefficients of absorption, with liquid either stirred or quiescent, and for all concentrations of gas phase. A similar mechanism will account for the formation of "liquid concentration films" for those cases in which the liquid film constitutes an important resistance.

It therefore follows that practical absorption apparatus which constantly creates new contacts between gas and liquid phases, thus minimizing the opportunity for gas and liquid films to form, will be especially effective, and will give much higher overall coefficients of absorption than will apparatus which brings gas and liquid into contact in such a way that the films have opportunity to develop.

